Supplemental Material
Photo-doping and In-gap Interface States across the Metal-Insulator Transition of $LaAlO_3/SrTiO_3$ heterostructures

Z. Ristic[1,2], R. Di Capua[1,3], F. Chiarella[1], G.M. De Luca[1], I. Maggio-Aprile[2], M. Radovic[4], and M. Salluzzo[1]

[1] CNR-SPIN, Complesso MonteSantangelo via Cinthia, I-80126 Napoli, Italy

[2] Departement de Physique de la Matiere Condensee, University of Geneva, 24 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

[3] Dipartimento S.pe.S., Università del Molise, Via De Sanctis, I-86100 Campobasso, Italy

[4] LSNS - EPFL, PH A2 354 (Batiment PH) Station 3 CH-1015 Lausanne, Switzerland

I. SCANNING TUNNELLING MICROSCOPY/SPECTROSCOPY OF THE BURIED INTERFACE

In the STM experimental set-up (see Fig.S1a), the bias voltage was applied to the tip (an electrochemical etched Iridium tip), and the contacts, directly sputtered onto the interface, were grounded. We performed several measurements, on several regions distant mm's one from the others, on two couples of twin 2uc and 4uc LAO/STO. The samples were studied as grown, without any surface treatment, and also after treatment in ethanol (99.9%) prior to the the introduction in UHV. We did not find substantial differences in the results, also after several weeks of exposition of the samples to UHV conditions. In order to maintain a tunneling regime in the bias voltage range investigated, we employed the high-gain amplification regime of our system, characterized by a 3×10^{11} V/A gain and a bandwidth of 200 Hz. The noise level has been experimentally determined to be of the order of 0.01 pA. We were able to work routinely with a tunneling current of 0.25 pA and bias voltages of 1 Volt. Typical exponential-like I_{tunnel} vs. sample-to-tip separation behavior were obtained with currents between 0.25 pA and 1 pA and bias voltages between +0.6 and +1.5 eV.

Tunneling electrons from and to the interface are exponentially attenuated by the $LaAlO_3$ barrier thickness (nominally 0.8 nm and 1.6 nm for the 2uc and 4uc samples, respectively). If states are available at the LAO surface, the tunneling contribution from those states is not attenuated by the LAO barrier, it is independent of the LAO thickness and consequently it would be not negligible. In the -1.5 to 1.5 V range investigated, we find that empty and occupied states of the LAO surface do not contribute to the tunneling current, as explained below [see also Z. Ristic, et al., EPL 93, 17004 (2011).].

Concerning unoccupied states, the conduction band minimum of $LaAlO_3$ (= +2.2 eV), is well above the investigate range [Z. Ristic, et al., EPL 93, 17004 (2011).]. Tunneling into unoccupied states of an insulator deposited on a metallic layer is possible if its thickness is below the electron inelastic mean free path (few nm's). Changing the thickness of LAO from 4uc to 6uc is not expected to reduce drastically the tunneling current, if tunneling into the unoccupied states of the LAO surface takes place. This was not the case, since we were unable to get stable conditions on 6 uc LAO/STO samples using a tip-bias voltages in the -1.5 to 1.5 V range.

If occupied states from the LAO surface contribute to tunneling, we should expect an asymmetric I-V characteristics, with a much higher tunneling current for negative bias voltages than for positive bias voltages, since tunneling into the LAO surface would be not attenuated by the LAO barrier. In Fig. S1b, we show a typical I vs V curve of a 4uc LAO/STO sample. We can see that the I-V curve is asymmetric, but in the opposite direction. Indeed, actually, the tunneling current is much higher for positive bias than for negative bias.

II. SURFACE AND INTERFACE MORPHOLOGY AND RELATIONSHIP WITH STRUCTURAL RESULTS

AFM and STM measurements under-light on 2uc LAO/STO interface show that the surface is incomplete (40% coverage) and that the interface is not atomically sharp.

In Fig.S2 we present typical AFM and STM analysis of the surface (AFM) and interface (STM) morphologies. Line profiles and coverage analysis on a single terrace showed that the LAO surface (AFM) is composed by atomic-layer steps, while the interface is relatively homogeneous but it is characterized by a corrugation of 1.5 unit cells (0.6 nm) on nanometer scales. Therefore, the interface is not atomically sharp and its corrugation is not correlated to the presence of incomplete layers on the LAO surface.

We performed a full structural refinement of the samples investigated, by fitting the structure factor vs. L of several (H, K) reflections measured by grazing incidence x-ray diffraction at the European Synchrotron Radiation Facility (ESRF) [see also ESRF report of experiment SI1853 at www.esrf.eu for details]. In Fig.S3 we report the occupation of La and Al cations of 2uc and 4uc samples. The data are in quantitative agreement with STM-AFM results, confirming that the surfaces were incomplete and that the interface intermixing extends for 1.5 unit cells, as reported also in (S. A. Pauli et al., Phys. Rev. Lett 106, 036101 (2011)).

III. SCANNING TUNNELLING MICROSCOPY AND SPECTROSCOPY OF 2 UNIT CELLS LAO/STO UNDER LIGHT

2uc LAO/STO samples are insulating under ambient conditions. Under visible light, the two point resistance between contacts placed at a distance of 0.5 mm is of the order of few $G\Omega$. In order to eliminate any systematic error related to these problems, we made several experimental checks. Any unwanted voltage drop between the contacts and the sample position below the tip would be directly seen in the I-V spectra as a voltage shift. If there is local charging, this shift is expected to increase as function of time during the measurement, making it unstable. At an initial distance between the tip position and a contact of 0.5 mm, the shift of the local potential is expected to be of the order of 4 mV ($4 \times 10^9 V/A \times 10^{-12} A = 4mV$ for 1 pA of tunnelling current and resistance of R=4$G\Omega$). Moving the tip to another location, 1 mm apart, we should experience at most an additional shift of $8mV$. The I/V characteristics, on the other hand, showed little changes as function of the distance from the contacts and as function of time. Consequently, the data on 2uc LAO/STO under light were not substantially affected by charging, and the local potential of the sample at the tip position was very close to zero.

By switching off the light, on the other hand, we observed the development of an instability in the tunneling conditions. After several seconds (up to 1 minute), simply the tip crashed into the surface. Thus, charging effectively takes place when the sample is left in dark. Thus, this result shows that photodoping, at room temperature, decreases the sample resistance of insulating 2uc LAO/STO samples.

IV. ANALYSIS OF THE SPECTROSCOPIC MAPS

Spectroscopy maps were acquired at room temperature. One complete spectroscopy map at high resolution (256 pixels x 256 pixels) required at least 14 hours of acquisition. In order to study the local electronic properties, we used the whole set of I(V) and (dI/dV) spectroscopy data to determine the main spectroscopic characteristic of the samples. In particular we draw our attention to the 4uc LAO/STO samples, which show inhomogeneities in the spectroscopic maps, as shown in Fig.S4 .

To classify the differences in the spectra between regions showing such inhomogeneities, instead of considering only a single $(dI/dV)/(I/V)$, $\propto LDOS$, map acquired at an arbitrarily chosen bias voltage, we used a more general approach, i.e. a classification algorithm. One of such techniques is the K-means clustering algorithm. It is commonly used in computer vision as a form of image segmentation resulting in border detection and object recognition (Anderson, T.W. An introduction to multivariate statistical analysis. Wiley, New York, 1958, (1984).). The unique input to the algorithm is the number of classes in which we consider the data divided, which, in the specific example considered in the paper, are simply three classes belonging to the different, red, blue, and cyan regions taken from the spectroscopy $(dI/dV)/(I/V)$ map measured at -1.3 V on 4uc LAO/STO [Fig. 2d and Fig. 3b of the paper].

The other approach used to highlight the inhomogeneities observed on the LAO/STO interface, was to look for a gap-map, i.e. by determining a gap from the dI/dV measurements. We used a threshold criteria for this purpose, and in particular, based on the dI/dV average spectra on the map shown in the see inset of Fig.2a and 2d of the paper) we established that an appropriate choice for the threshold was 2% of the stabilization tunnelling conductance, i.e. 0.01 pA/V in the present case. In Fig. S5c we show the cross correlation image obtained between the gap map of Fig.S5a and the LDOS map at -1.3V of Fig.S5b. We can see that there is a very good correlation between the two maps, so that the presence of regions with a peak in the LDOS at -1.3 V, is related to the opening of a small gap in the spectra.

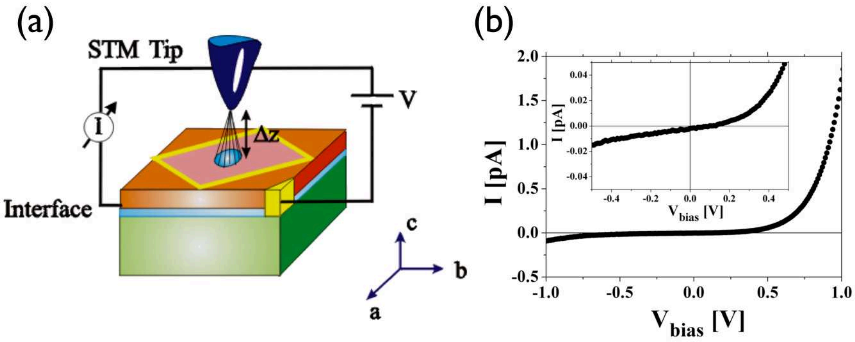

Fig. S1: (a) Schematics of the experimental set-up during the STM measurements; (b) I vs V characteristics of a 4uc LAO/STO sample, averaged on an area of 32x32 nm^2, showing the asymmetry as function of the bias. In the inset the same data are shown in the region around the Fermi level.

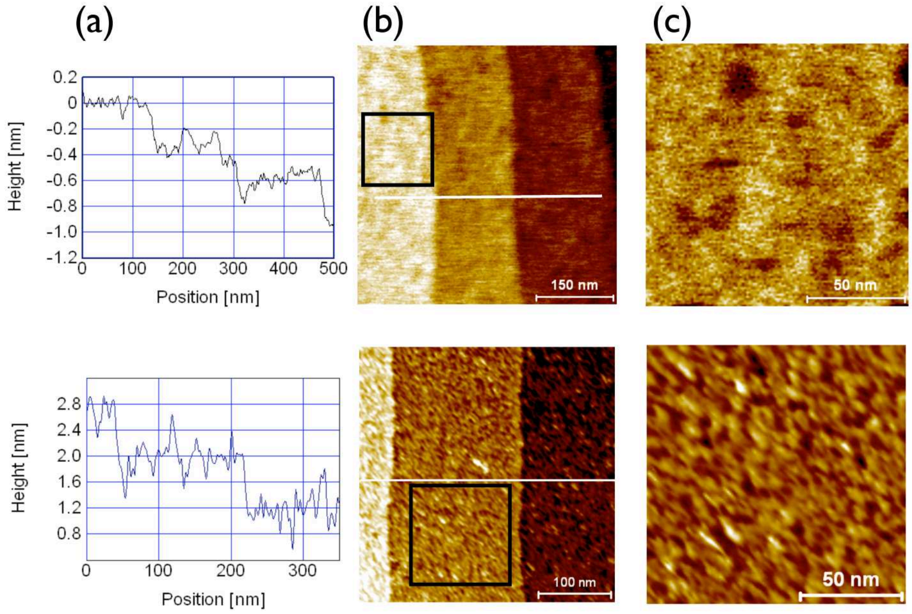

Fig. S2: (a) Z-height line-profiles, (b) topographies and (c) zoom images on the terraces obtained by contact AFM (upper panels) and STM (bottom panels) on a 2uc LAO/STO sample under light. In panels (b), the square rectangles and the white-lines represent respectively the areas and the profile regions corresponding to (a) and (c). The AFM image is a topography of the LAO surface, while the STM image is a topography of the interface. There is no correspondence between the details of the AFM and STM topographies within each terrace. The roughness of a single terrace belonging to the interface is between 0.6-0.8 nm (1.5-2 uc).

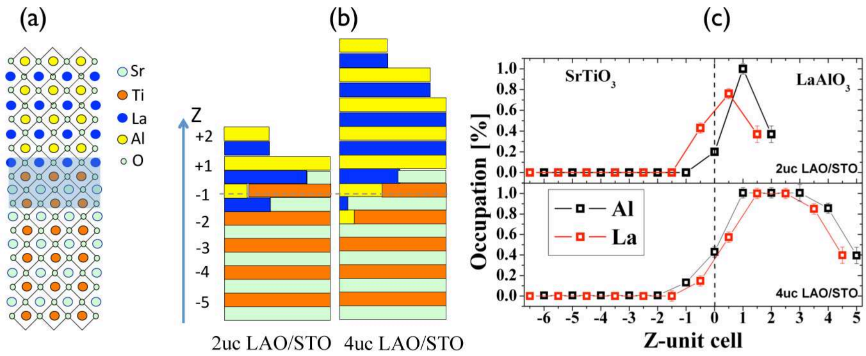

Fig. S3: (a) Ideal drawing of the layers sequence in the LAO/STO system, and (b) schematic of the occupancies obtained from the fit of Grazing incidence x-ray diffraction structural data. The color code used in (b) corresponds to the one used in (a) for each cation; (c) Al (red symbols) and La (black symbols) occupancies of 2uc (upper panel) and 4uc (bottom panel) LAO/STO. The samples measured by GXID were also measured by STM, as shown in Fig.S2.

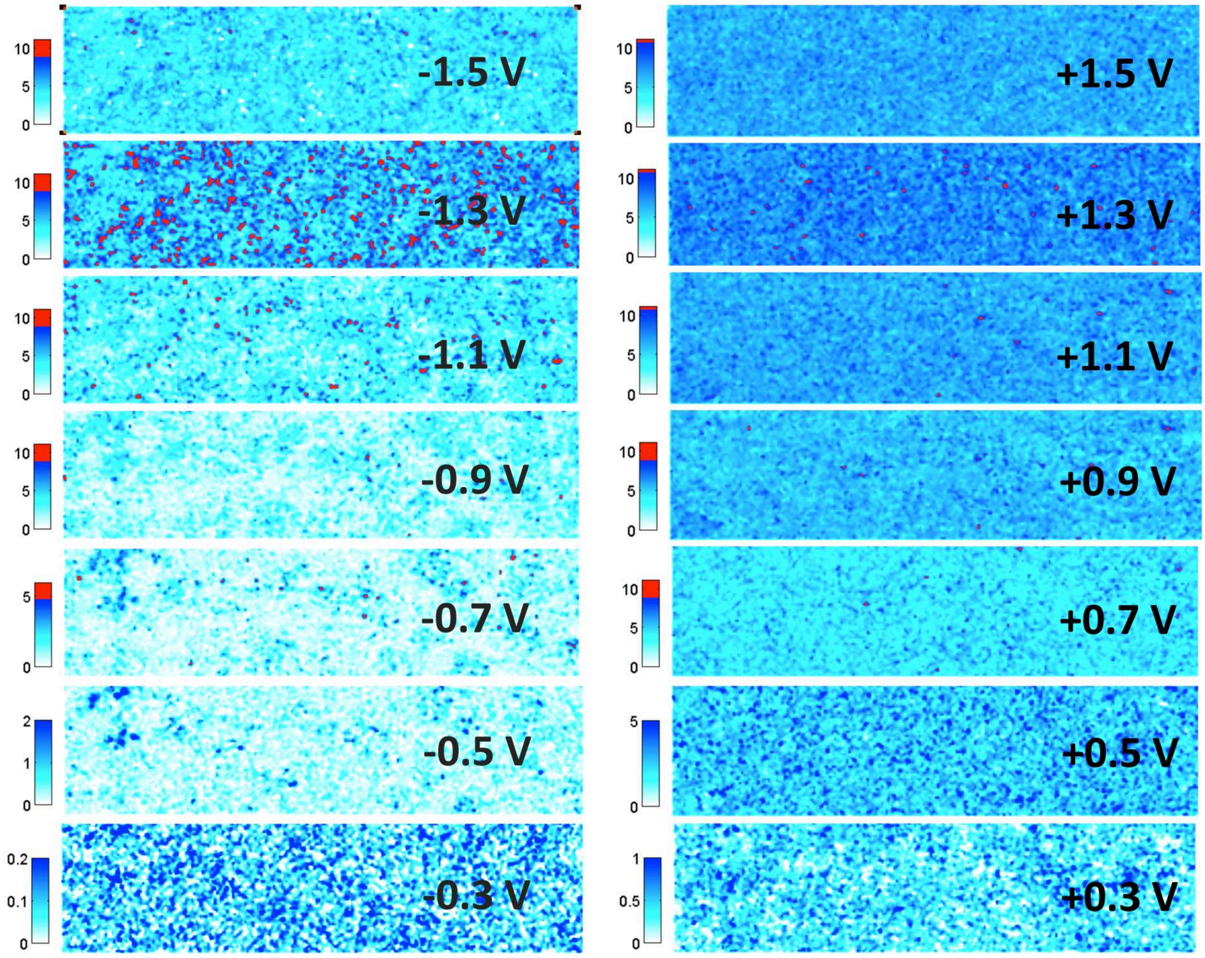

Fig. S4: $(dI/dV)/(I/V)$ maps at different tunneling bias voltages (as indicated in the images) showing the appearance of nanometer scale electronic inhomogeneities in conducting LAO/STO. The non-linear color-map scale used is fixed in images acquire at bias voltage between -1.0 V and -1.5V to emphasizes the enhanced normalized conductance around -1.3 V, while all the others have been rescaled in order to increase the contrast, in particular the one at a bias close to the Fermi level.

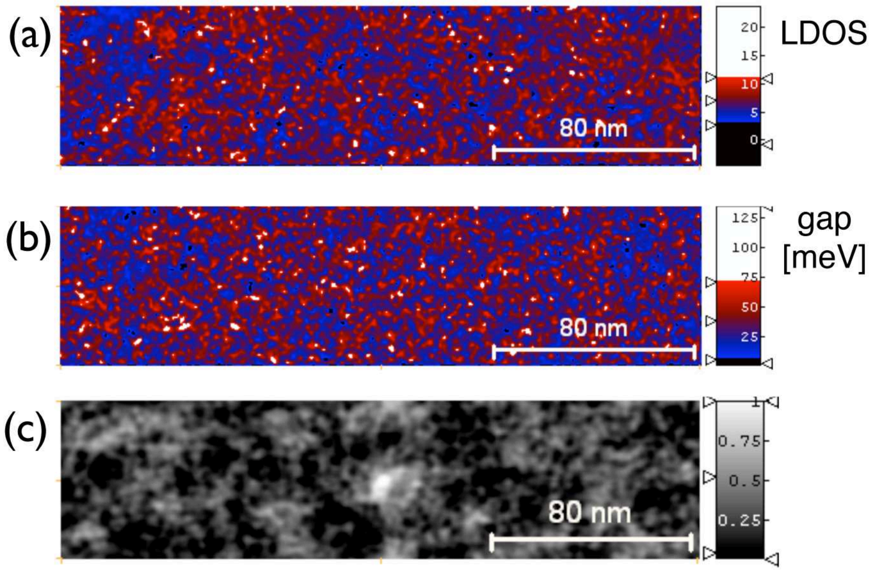

Fig. S5: (a) $(dI/dV)/(I/V)$ map at -1.3 V, (b) gap map and (c) cross correlation image between (a) and (b) . The non-linear color-map scale used in (a) and (b) overemphasizes the presence of inhomogeneities.